FUEL PROCESSING SYSTEM AND IMPROVED FEEDSTOCK THEREFOR

Related Application

This application claims priority to co-pending U.S. Provisional Patent Application Serial No. 60/248,236, which was filed on November 13, 2000, is entitled "Fuel Processing System and Improved Feedstock Therefor," and the complete disclosure of which is hereby incorporated by reference for all purposes.

Field of the Invention

The present invention relates generally to fuel processing systems, and more particularly to an improved feedstock for fuel processing systems and fuel processing systems utilizing this feedstock.

Background and Summary of the Invention

A fuel processing system includes a fuel processor that produces hydrogen gas from a carbon-containing feedstock. Examples of suitable fuel processors include steam reformers and autothermal reformers that utilize a reforming catalyst to produce hydrogen gas from the carbon-containing feedstock and water. The system may, but does not necessarily, include a fuel cell stack that produces an electrical current from the hydrogen gas produced by the fuel processor.

Examples of suitable carbon-containing feedstocks include hydrocarbons and alcohols. Methanol is an ideal feedstock for use in a fuel processing system, especially when the hydrogen gas produced in the fuel

processor is delivered to a low-temperature fuel-cell stack, such as fuel cell stacks that include proton-exchange membrane (PEM) fuel cells or alkaline fuel cells.

However, methanol also poses health hazards because it is a toxic alcohol (by inhalation of vapors, contact with the liquid, and ingestion of the liquid). Methanol also has very little odor. Because of this, it is difficult to smell methanol if it is spilled or leaks from a storage device, fuel processor, transport conduit, or the like. Therefore, there is a need for a suitable method for detecting methanol that leaks, spills, or is otherwise unintentionally released. Conventional odorants used with natural gas are not suitable for use in fuel processing systems because these odorants are alkyl thiols that poison the reforming catalyst, thereby destroying the utility of the fuel processor.

Summary of the Invention

The present invention is directed to an improved feedstock for fuel processing systems, and fuel processing systems incorporating the same. The fuel processing system includes a fuel processor adapted to produce a product hydrogen stream from a carbon-containing feedstock. The fuel processing system may also include a fuel cell stack adapted to produce an electric current from the product hydrogen stream. The feedstock is at least substantially formed of a hydrocarbon or alcohol. In an exemplary embodiment, the feedstock includes methanol. The feedstock also includes at least one odorant adapted to produce a strong and characteristic odor, even when present in only low concentrations. The

odorant, or odorants, are selected to be free or at least sufficiently free from compounds that will poison the catalyst used in the fuel processor.

Brief Description of the Drawings

Fig. 1 is a schematic diagram of a fuel processing system according to the present invention.

Fig. 2 is a schematic diagram of another fuel processing system according to the present invention.

Fig. 3 is a schematic diagram of a fuel processor suitable for use in the system of Fig. 1.

Fig. 4 is a schematic diagram of another fuel processor suitable for use in the system of Fig. 1.

Detailed Description and Best Mode of the Invention

A fuel processing system according to the present invention is shown in Fig. 1 and generally indicated at 10. System 10 includes at least one fuel processor 12 that is adapted to produce a product hydrogen stream 14 containing hydrogen gas from a feed stream 16 containing a carbon-containing feedstock 18. Feed stream 16 may be delivered to fuel processor 12 via any suitable mechanism. Feedstock 18 includes at least one hydrocarbon or alcohol. Examples of suitable hydrocarbons include methane, propane, natural gas, diesel, kerosene, gasoline and the like. Examples of suitable alcohols include methanol, ethanol, and polyols such as ethylene glycol and propylene glycol.

Fuel processor 12 may produce hydrogen gas from carbon-containing feedstock 18 through any suitable mechanism. Examples of suitable mechanisms include steam reforming and autothermal reforming, in which reforming catalysts are used to produce hydrogen gas from carbon-containing feedstock 18 and water 20. Another suitable mechanism for producing hydrogen gas is catalytic partial oxidation of an alcohol or hydrocarbon.

Although only a single feed stream 16 is shown in Fig. 1, it should be understood that more than one stream 16 may be used and that these streams may contain the same or different components. When carbon-containing feedstock 18 is miscible with water, the feedstock is typically delivered with the water component of feed stream 16, such as shown in Fig. 1. When the carbon-containing feedstock is immiscible or only slightly miscible with water, these components are typically delivered to fuel processor 12 in separate streams such as shown in Fig. 2.

Fuel processing system 10 may, but does not necessarily, further include at least one fuel cell stack 22. Fuel cell stack 22 contains at least one, and typically multiple, fuel cells 24 adapted to produce an electric current from the portion of the product hydrogen stream delivered thereto. Examples of suitable fuel cells include proton exchange membrane (PEM) fuel cells and alkaline fuel cells. Some or all of stream 14 may additionally, or alternatively, be delivered, via a suitable conduit, for use in another hydrogen-consuming process, burned for

fuel/heat, or stored for later use. Examples of suitable storage mechanisms include pressurized tanks and hydride beds.

As discussed above, carbon-containing feedstock 18 may be any suitable hydrocarbon or alcohol. When fuel processing system 10 includes a fuel cell stack, a preferred feedstock is methanol, and more particularly, fuel-cell grade methanol. Generally, catalysts that are used for conducting the water-gas shift reaction are suitable for steam reforming methanol. Commonly used (and commercially available) methanol steam-reforming catalysts consist of mixtures of copper and zinc oxide, and copper and chromium oxide. These catalyst formulations are very rapidly and completely poisoned by compounds of sulfur, compounds of phosphorous, volatile heavy metals (e.g., cadmium, mercury), and compounds of heavy metals. Therefore, the methanol is preferably free from these compounds so that the reforming catalyst is not poisoned. Similarly, other carbon-containing feedstocks should be sufficiently free from these or other compounds that will poison the reforming or other catalysts used to produce hydrogen gas therefrom.

Because methanol is toxic, it poses a health hazard if ingested or inhaled. Because methanol is generally odorless, it is not readily identified or noticed if spilled or unintentionally discharged from the fuel processing system. Therefore, carbon-containing feedstock 18 preferably includes one or more odorants 26.

The odorant should be volatile and should be completely, or sufficiently, free of compounds that will impair the operation of fuel processing system 10, such as compounds that will poison the catalyst used in fuel processor 12. For example, odorants used with reforming catalysts should include only trace, and preferably are free of, sulfur, phosphorous and heavy metals. By "volatile," it is meant that the odorant has a boiling point of less than approximately 300° C. Typically, but not necessarily, these compounds will also have a low molecular weight. By "low molecular weight," it is meant that these compounds have a molecular weight less than approximately 1000. Odorant 26 should be partially, or completely, miscible with methanol or the other carbon-containing feedstock with which the odorant is used.

Odorant 26 should produce a strong and detectable odor, even when the odorant is present in low concentrations. Preferably, the odorant produces a characteristic odor. Even more preferably, the odorant produces a distasteful odor. By "characteristic odor," it is meant that the odor is readily detectable in the environment surrounding the fuel processing system by not being an odor commonly present in such an environment. Therefore, even when odorant 26 is used with a carbon-containing feedstock that itself has an odor, the characteristic smell of the odorant will be detectable. By "distasteful," it is meant that the odor smells rotten, such as smelling like rotting eggs, fish, flesh, etc. This is particularly useful when the carbon-containing feedstock is toxic or otherwise hazardous if ingested because the distasteful smell of the odorant will disincline

ingestion of the carbon-containing feedstock/odorant mixture, even if the individual does not know that the mixture is toxic or otherwise hazardous.

Any suitable odorant meeting the criteria set forth herein may be used. Examples of suitable odorants 26 include organic amines with at least one amine functional group. The following table lists several candidate organic amines and their melting and boiling points.

Table 1
Physical Properties of Organic Amines

Odorant	Melting Point (°C)	Boiling Point (°C)
Trimethylamine	-117	3-4
Triethylamine	-115	88.8
Tripropylamine	-93.5	155-158
n-Butylamine	-50.5	77.9
n-Pentlyamine	-50	104
n-Hexylamine	-23	131-132
n-Heptylamine	-23	154-156
n-Octylamine	-5	175-177
n-Decylamine	12-14	216-218
1,3-Diaminopropane	-12	140
1,4-Diaminobutane	27-28	158-160
1,5-Diaminopentane	9	178-180
1,7-Diaminoheptane	27-29	147-149

All of these odorants have a characteristically unpleasant odor that is detectable at very low concentrations. For instance, trimethylamine has a characteristic "rotten fish" odor that is easily smelled when trimethylamine is dissolved in methanol/water mixtures at a concentration of 10 ppm (parts per million by volume). Trimethylamine is available as a 40% solution in water from Aldrich Chemical Co. of Milwaukee, Wisconsin.

Experiments using trimethylamine doped methanol/water solution (10 ppm trimethylamine added to a methanol/water mixture containing 67vol% methanol and 33vol% water) have shown that the activity of a commercial copper/zinc oxide reforming catalyst (G66B, sold by Süd-Chemie of Louisville, Kentucky) is unaffected by the trimethylamine.

Although these volatile organic amines are effective odorants, they also offer an additional advantage of deterring human consumption due to their distasteful smell. In particular, trimethylamine smells like rotten fish, whereas 1,4-diaminobutane and 1,5-diaminopentane have smells characterisitic of rotten flesh (hence their trivial names of putrescine and cadaverine, respectively).

As discussed, an example of a suitable fuel processor 12 is a steam reformer. An example of a suitable steam reformer is shown in Fig. 3 and indicated generally at 30. Reformer 30 includes a reforming, or hydrogen-producing, region 32 that includes a steam reforming catalyst 34. Alternatively, reformer 30 may be an autothermal reformer that includes an autothermal reforming catalyst. In region 32, a hydrogen-containing stream 36 is produced from the water and carbon-containing feedstock forming feed stream(s) 16. The hydrogen-containing stream typically contains impurities, and therefore is delivered to a separation region, or purification region, 38, where the stream is purified. In separation region 38, the hydrogen-containing stream is separated into one or more byproduct streams 40 and a hydrogen-rich stream 42 by any suitable

pressure-driven separation process. In Fig. 3, hydrogen-rich stream 42 is shown forming product hydrogen stream 14.

An example of a suitable structure for use in separation region 38 is a membrane module 44, which contains one or more hydrogen permeable metal membranes 46. An example of a suitable membrane module formed from a plurality of hydrogen-selective metal membranes is disclosed in U.S. Patent No. 6,221,117, which was filed on April 13, 1999 as U.S. Patent Application Serial No. 09/291,447, is entitled "Fuel Processing System," and the complete disclosure of which is hereby incorporated by reference. In that application, a plurality of generally planar membranes are assembled together into a membrane module having flow channels through which an impure gas stream is delivered to the membranes, a purified gas stream is harvested from the membranes and a byproduct stream is removed from the membranes. Gaskets, such as flexible graphite gaskets, are used to achieve seals around the feed and permeate flow channels. Other examples are disclosed in U.S. Patent Application Serial No. 09/812,499, which was filed on March 19, 2001, is entitled "Hydrogen-Selective Metal Membrane Modules and Method of Forming the Same", and the complete disclosure of which is hereby incorporated by reference; and in U.S. Patent Application Serial No. 09/967,172, which was filed on September 27, 2001, is entitled "Hydrogen Purification Devices, Components and Fuel Processing Systems Containing The Same", and the complete disclosure of which is hereby

incorporated by reference. Other suitable fuel processors are also disclosed in the incorporated patent applications.

The thin, planar, hydrogen-permeable membranes are preferably composed of palladium alloys, most especially palladium with 35 wt% to 45 wt% copper. These membranes are typically formed from a thin foil that is approximately 0.001 inches thick. It is within the scope of the present invention, however, that the membranes may be formed from hydrogen-selective metals and metal alloys other than those discussed above, hydrogen-permeable and selective ceramics, or carbon compositions. The membranes may have thicknesses that are larger or smaller than discussed above. For example, the membrane may be made thinner, with commensurate increase in hydrogen flux. The hydrogen-permeable membranes may be arranged in any suitable configuration, such as arranged in pairs around a common permeate channel as is disclosed in the incorporated patent application. The hydrogen permeable membrane or membranes may take other configurations as well, such as tubular configurations.

Another example of a suitable pressure-separation process is pressure swing absorption (PSA). Therefore, region 38 may alternatively include suitable structure for performing pressure swing absorption.

Reformer 30 may, but does not necessarily, further include a polishing region 48, such as shown in Fig. 4. Polishing region 48 receives hydrogen-rich stream 42 from separation region 38 and further purifies the stream by reducing the concentration of, or removing, selected compositions therein. For

example, when fuel processing system 10 includes a fuel cell stack, or when product hydrogen stream 14 is intended for use in a fuel cell stack, compositions that may damage the fuel cell stack, such as carbon monoxide and carbon dioxide, may be removed from the hydrogen-rich stream. Region 48 includes any suitable structure for removing or reducing the concentration of the selected compositions in stream 42. For example, when the product stream is intended for use in a PEM fuel cell stack or other device that will be damaged if the stream contains more than determined concentrations of carbon monoxide or carbon dioxide, it may be desirable to include at least one methanation catalyst bed 50. Bed 50 converts carbon monoxide and carbon dioxide into methane and water, both of which will not damage a PEM fuel cell stack. Polishing region 48 may also include another hydrogen-producing device 52, such as another reforming catalyst bed, to convert any unreacted feedstock into hydrogen gas. In such an embodiment, it is preferable that the second reforming catalyst bed is upstream from the methanation catalyst bed so as not to reintroduce carbon dioxide or carbon monoxide downstream of the methanation catalyst bed.

Industrial Applicability

The present invention is applicable in any fuel processing system in which hydrogen gas is produced from a carbon-containing feedstock. The invention is particularly useful when the carbon-containing feedstock is methanol, although it may be used with other hydrocarbons and alcohols.

It is believed that the disclosure set forth above encompasses multiple distinct inventions with independent utility. While each of these inventions has been disclosed in its preferred form, the specific embodiments thereof as disclosed and illustrated herein are not to be considered in a limiting sense as numerous variations are possible. The subject matter of the inventions includes all novel and non-obvious combinations and subcombinations of the various elements, features, functions and/or properties disclosed herein. Similarly, where the claims recite "a" or "a first" element or the equivalent thereof, such claims should be understood to include incorporation of one or more such elements, neither requiring nor excluding two or more such elements.

It is believed that the following claims particularly point out certain combinations and subcombinations that are directed to one of the disclosed inventions and are novel and non-obvious. Inventions embodied in other combinations and subcombinations of features, functions, elements and/or properties may be claimed through amendment of the present claims or presentation of new claims in this or a related application. Such amended or new claims, whether they are directed to a different invention or directed to the same invention, whether different, broader, narrower or equal in scope to the original claims, are also regarded as included within the subject matter of the inventions of the present disclosure.